

OXFORD CAMBRIDGE AND RSA EXAMINATIONS

Advanced GCE

CHEMISTRY

2814

Chains, Rings and Spectroscopy

Wednesday **21 JANUARY 2004** Morning 1 hour 30 minutes

Candidates answer on the question paper.

Additional materials:

Data Sheet for Chemistry

Scientific calculator

Candidate Name	Centre Number	Candidate Number											
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TIME 1 hour 30 minutes

INSTRUCTIONS TO CANDIDATES

- Write your name in the space above.
- Write your Centre number and Candidate number in the boxes above.
- Answer **all** the questions.
- Write your answers in the spaces provided on the question paper.
- Read each question carefully and make sure you know what you have to do before starting your answer.

INFORMATION FOR CANDIDATES

- The number of marks is given in brackets [] at the end of each question or part question.
- You will be awarded marks for the quality of written communication where this is indicated in the question.
- You may use a scientific calculator.
- You may use the *Data Sheet for Chemistry*.
- You are advised to show all the steps in any calculations.

FOR EXAMINER'S USE		
Qu.	Max.	Mark
1	21	
2	14	
3	10	
4	19	
5	15	
6	11	
TOTAL	90	

This question paper consists of 17 printed pages and 3 blank pages.

BLANK PAGE

Answer **all** the questions.

1 An unknown compound **A** is thought to be either an aldehyde or a ketone.

(a) The molecular formula of compound **A** is deduced with the help of the molecular ion peak of its mass spectrum.

(i) What information does the *molecular ion peak* of a mass spectrum give?

.....[1]

(ii) Where on a mass spectrum is the molecular ion peak found?

.....[1]

(b) The molecular formula of compound **A** is found to be $C_5H_{10}O$.

Show the **four** possible structural isomers of $C_5H_{10}O$ that are aldehydes.

[4]

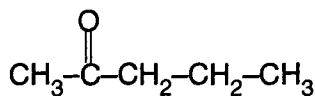
(c) Describe how you would carry out a simple **chemical** test which can be used to distinguish between aldehydes and ketones. Give the expected result in each case.

.....

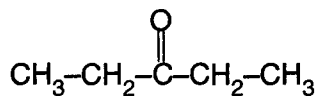
result for an aldehyde

result for a ketone[4]

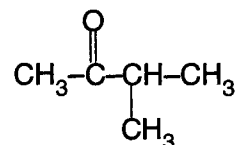
- (d) This test indicates that compound **A** is in fact a ketone. Three possible ketones with molecular formula $C_5H_{10}O$ are shown below.



pentan-2-one



pentan-3-one



methylbutanone

A solution of 2,4-dinitrophenylhydrazine is added to compound **A**.

- (i) State what you would see.

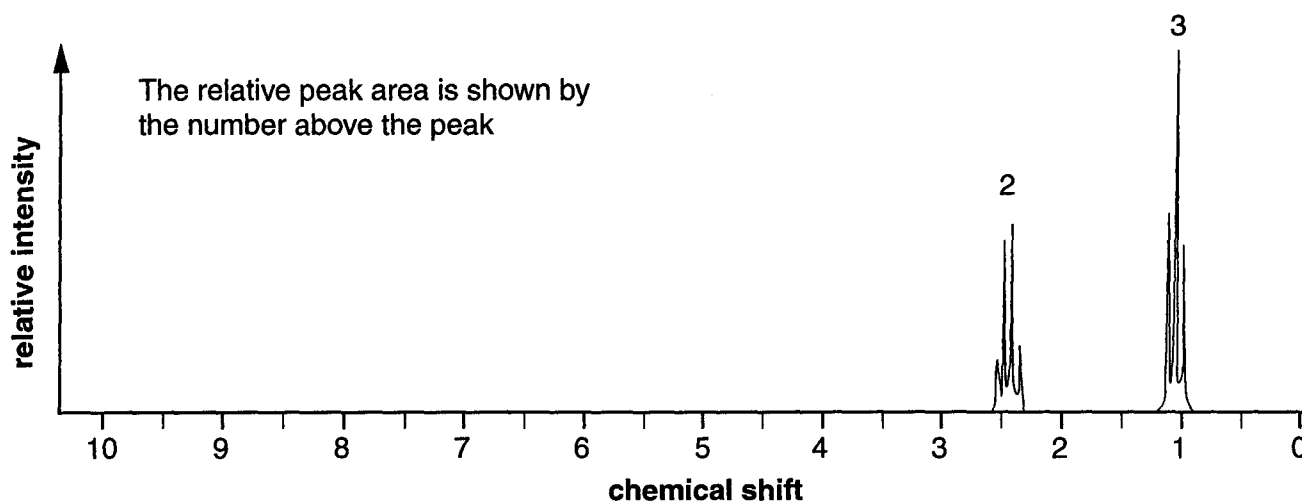
.....
[2]

- (ii) Describe the method, which does **not** involve spectroscopy, that uses the product from this test to distinguish between the possible structures of compound **A**.

.....

[2]

- (e) The structure of compound **A** can also be identified from its n.m.r. spectrum shown below.



- (i) Explain how this spectrum confirms that compound **A** is **not** an aldehyde.

.....
[1]

- (ii) Use the n.m.r. spectrum to deduce which of the ketones shown in part (d) is the correct structure of compound **A**.

Explain your reasoning clearly, identifying which part of the molecule is responsible for each peak.

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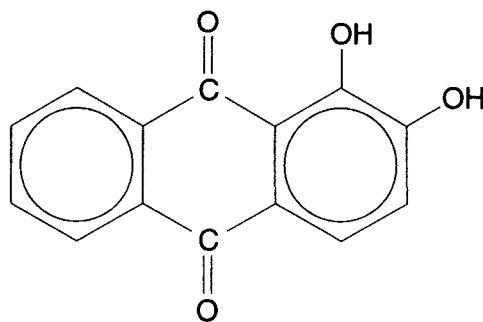
.....

.....

.....[6]

[Total: 21]

- 2 Alizarin is a red coloured compound used to dye fabrics. Its structure is shown below.



alizarin

- (a) Apart from the benzene ring, name **two** different functional groups in this molecule.

..... and [2]

- (b) (i) Deduce the molecular formula of alizarin from its structure given above.

..... [2]

- (ii) To dye a piece of cloth with alizarin, an aqueous solution needs to be made to a concentration of about $0.015 \text{ mol dm}^{-3}$.

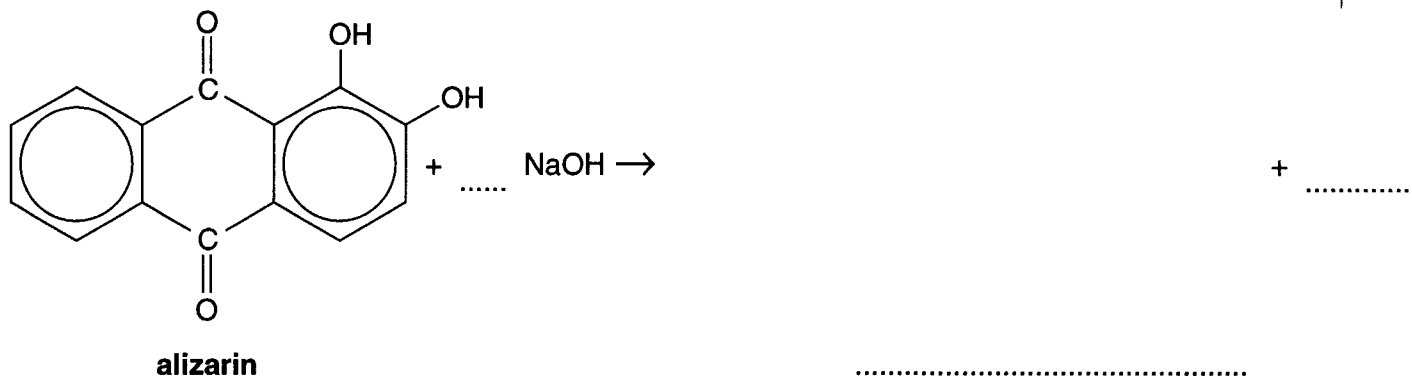
Calculate the mass of alizarin present in 800 cm^3 of a $0.015 \text{ mol dm}^{-3}$ solution.

M_r of alizarin = 240.

mass of alizarin = g [2]

- (c) Alizarin reacts with cold aqueous sodium hydroxide.

Complete the equation to show the reaction of alizarin with an **excess** of aqueous sodium hydroxide. Show clearly the structure of the organic product and balance the equation.



[3]

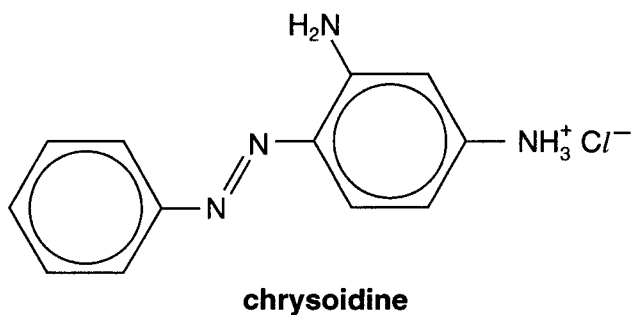
- (d) Infra-red spectroscopy can be used to identify bonds in dye molecules such as alizarin.

State the particular bonds in alizarin that give rise to characteristic peaks on its infra-red spectrum. Give the wavenumber range for each peak.

.....

[4]

- (e) The structure of another dye called chrysoidine is shown below.



Chrysoidine is described as an azo dye, but alizarin is **not**.

Draw a circle around the part of the molecule in chrysoidine that identifies it as an azo dye. [1]

[Total: 14]

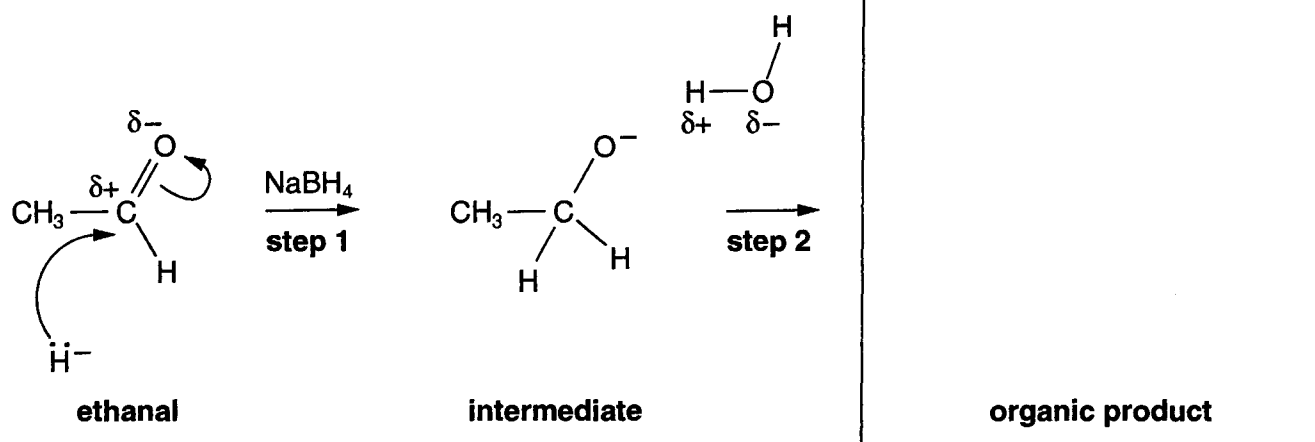
- 3 Ethanal, CH_3CHO , can be reduced using an aqueous solution of sodium borohydride, NaBH_4 , as the reducing agent.

(a) Write a balanced equation for this reaction using the symbol $[\text{H}]$ to represent the reducing agent.

.....[2]

(b) This is a nucleophilic addition reaction in which the nucleophile can be represented as a hydride ion, H^- .

A mechanism for the reaction is shown below.



- (i) Add 'curly arrows' to the mechanism to show how the intermediate reacts with the water molecule in **step 2**. [2]
- (ii) Draw the structure of the organic product of this reaction in the box above. [1]
- (iii) What is meant by the term *nucleophile*? [1]
-[1]
- (iv) Describe in words exactly what is happening to the electron pairs and bonds in **step 1** of the mechanism above. [3]
-
-
-
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-
-
-[3]

- (c) It is also possible to reduce ethanal to the same product using hydrogen gas, H_2 , in the presence of a catalyst. This reaction does **not** go by a nucleophilic mechanism.

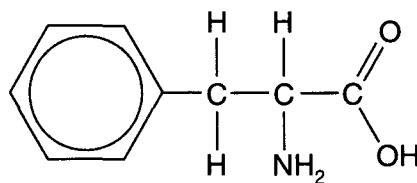
Explain why hydrogen gas cannot act as a nucleophile.

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.....[1]

[Total: 10]

- 4 Phenylalanine is a naturally occurring α -amino acid. Its structure is shown below.



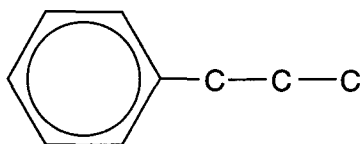
phenylalanine

- (a) State the general formula of an α -amino acid.

..... [1]

- (b) Phenylalanine exists at pH 7 in the body as a zwitterion.

Complete the displayed formula of phenylalanine below to show the zwitterion of phenylalanine.



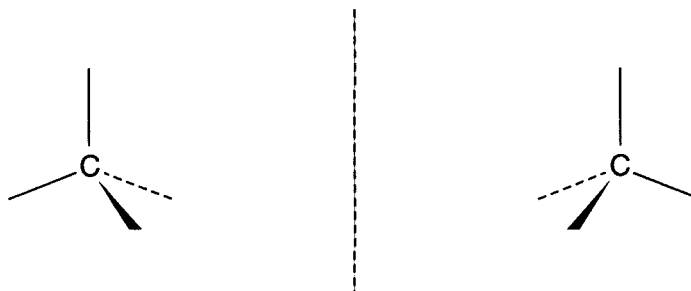
[2]

- (c) Phenylalanine has two stereoisomers.

- (i) What is the name of the type of stereoisomerism shown by phenylalanine?

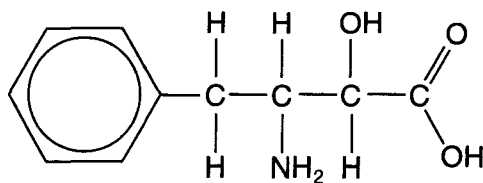
.....[1]

- (ii) Complete the structures below to show the three-dimensional arrangement of the two stereoisomers of phenylalanine.



[2]

- (d) Compound **G** is used to make a drug that inhibits the action of the HIV virus.



compound **G**

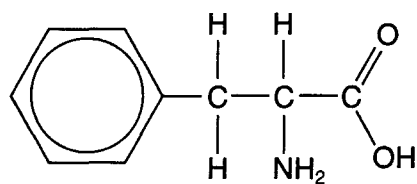
Compound **G** is a β -amino acid, whereas most naturally occurring amino acids are α -amino acids.

State **three** differences between the structures of compound **G** and phenylalanine.

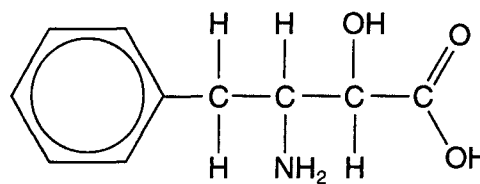
.....

[3]

- (e) Compound **G** can be synthesised in three steps from phenylalanine as shown below.



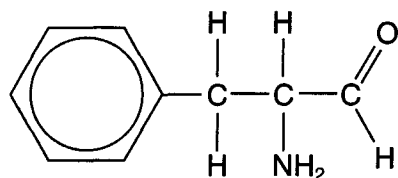
phenylalanine



compound **G**

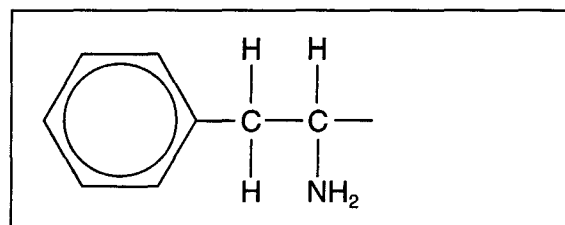
reduction

hydrolysis



compound **E**

HCN/KCN



compound **F**

- (i) Complete the structure of compound **F** in the box above.

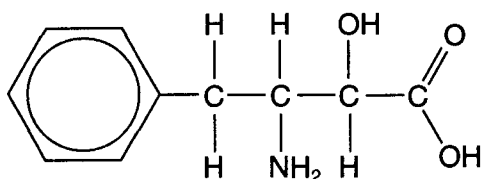
[1]

- (ii) Explain why reaction of a carbonyl compound, such as compound **E**, with HCN/KCN is particularly useful in the synthesis of organic compounds.

.....
[1]

- (f) Compound **G** contains two chiral centres and its stereochemistry has been found to be significant in the action of the drug. The drug works because it has the right shape to inhibit an enzyme that is needed by the HIV virus.

- (i) Identify the **two** chiral centres in compound **G** by placing an asterisk * by the appropriate atoms on this structure of **G**.



compound **G**

[2]

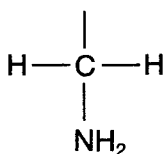
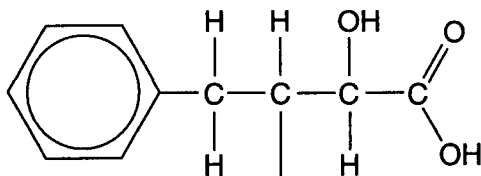
- (ii) State whether the compound **G** made by this method will contain a single stereoisomer or a mixture containing more than one stereoisomer. Explain your answer.

.....

[1]

- (g) To finally make the drug, compound **G** is made into a dipeptide by combining it with an α -amino acid such as glycine, $\text{H}_2\text{NCH}_2\text{COOH}$.

Complete the diagram to show the displayed formula of the peptide bond between compound **G** and glycine.



[2]

- (h) Discuss the possible **disadvantages** of producing an anti-HIV drug which contains more than one stereoisomer.

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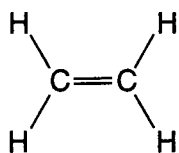
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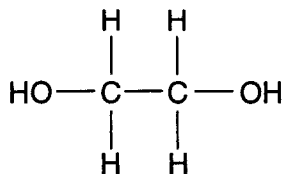
[Total: 19]

- 5 Clear plastic drink bottles are usually made from either HDPE (high-density polythene) or from PET (polyethylene terephthalate). HDPE is an **addition polymer** and is used for softer bottles, whereas PET is a **condensation polymer** used for bottles needing a greater rigidity. PET is also known as *Terylene* when it is used to make fibres.

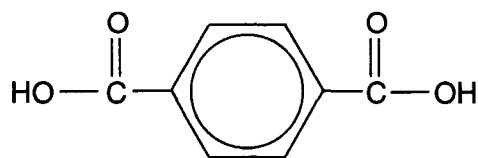
The monomers used to make these two polymers are shown below.



ethene



ethane-1,2-diol



benzene-1,4-dicarboxylic acid

- (a) In this question, one mark is available for the quality of written communication.

Using HDPE and PET as your examples, explain the difference between *addition* and *condensation* polymerisation.

Include equations to show the polymerisation reaction forming each polymer and clearly show the repeat unit in HDPE and PET.

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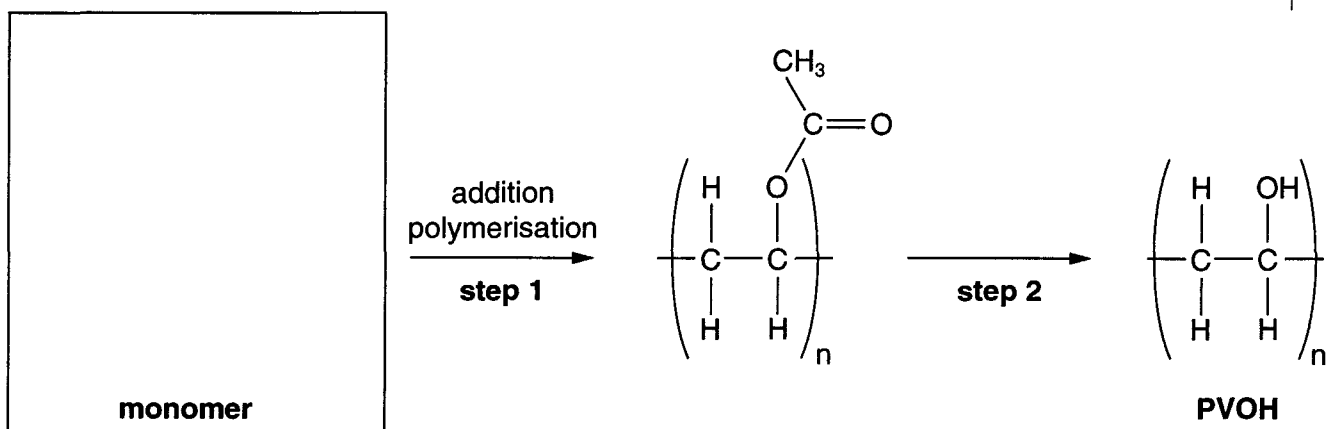
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[7]

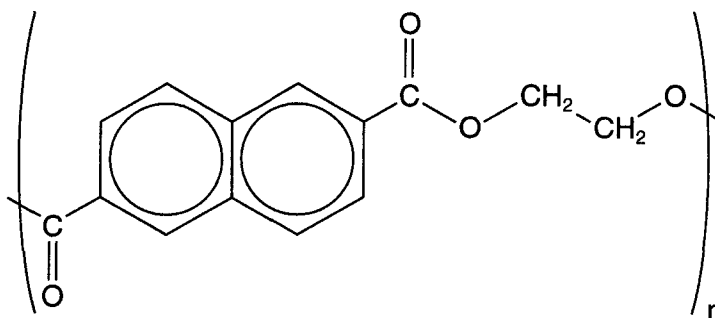
Quality of Written Communication [1]

- (b) Bottles made from PET are often used to contain carbonated drinks. However PET allows the gas to escape slowly. A layer of another polymer can be included to decrease the gas leakage. One such polymer is PVOH (polyvinyl alcohol). This is manufactured in two steps as shown below.



- (i) In the box above, draw the structure of the monomer used in **step 1**. [1]
- (ii) **Step 2** involves hydrolysis of the ester in the side chain.
- State the reagents and conditions required for **step 2**.
- reagents
- conditions[3]
- (iii) Another compound is formed in **step 2**. Identify this compound.
-[1]

- (c) Research is being carried out to find alternatives to PET that do not allow gases to escape. The formula of the repeat unit of one possible condensation polymer is shown.



Deduce the structures of the **two** monomers from which this polymer could be made.

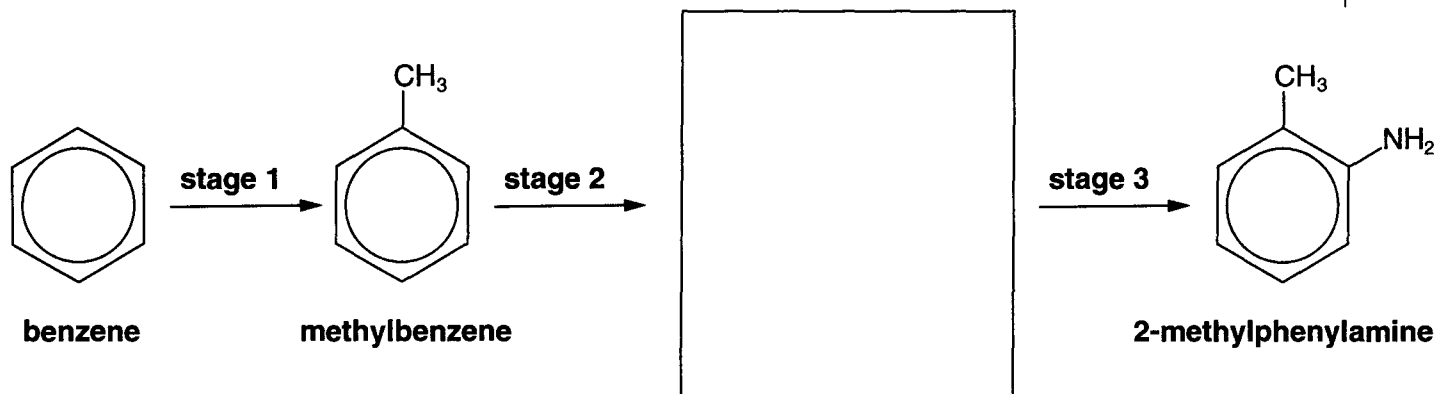
[2]

[Total: 15]

[Turn over]

- 6 2-Methylphenylamine is used in the large-scale production of a variety of dyes, pesticides and pharmaceuticals.

It can be manufactured from benzene in three stages, as shown below.



- (a) The conversion of benzene to methylbenzene in **stage 1** needs another reagent and a halogen carrier.
- (i) Identify the reagent.[1]
- (ii) Suggest a suitable halogen carrier.[1]
- (b) In the box above, draw the structure of the compound formed in **stage 2**. [1]

- Outline how **stage 2** and **stage 3** can be carried out.

(You do not need to include details of the separation or purification of the compounds).

.....[7]

[Total: 11]

2814 Jan04